

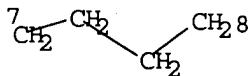
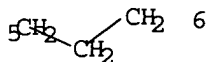
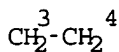
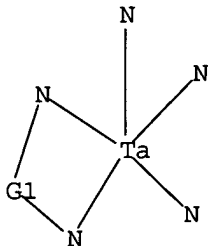
10/684,545

(FILE 'HOME' ENTERED AT 11:56:29 ON 01 MAR 2005)

FILE 'REGISTRY' ENTERED AT 11:56:46 ON 01 MAR 2005

L1 STRUCTURE UPLOADED  
L2 STRUCTURE UPLOADED

=> d 12  
L2 HAS NO ANSWERS  
L2 STR



G1 N,Si,[@1-@2],[@3-@4],[@5-@6],[@7-@8]

Structure attributes must be viewed using STN Express query preparation.

=> s 12  
SAMPLE SEARCH INITIATED 12:05:34 FILE 'REGISTRY'  
SAMPLE SCREEN SEARCH COMPLETED - 24 TO ITERATE

100.0% PROCESSED 24 ITERATIONS 0 ANSWERS  
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*  
BATCH \*\*COMPLETE\*\*  
PROJECTED ITERATIONS: 187 TO 773  
PROJECTED ANSWERS: 0 TO 0

L3 0 SEA SSS SAM L2

=> s 12 full  
FULL SEARCH INITIATED 12:05:41 FILE 'REGISTRY'  
FULL SCREEN SEARCH COMPLETED - 448 TO ITERATE

100.0% PROCESSED 448 ITERATIONS 0 ANSWERS  
SEARCH TIME: 00.00.01

L4 0 SEA SSS FUL L2

(FILE 'HOME' ENTERED AT 12:43:54 ON 01 MAR 2005)

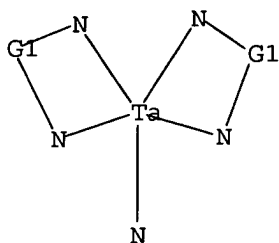
FILE 'REGISTRY' ENTERED AT 12:44:14 ON 01 MAR 2005

L1 STRUCTURE UPLOADED

=> d l1

L1 HAS NO ANSWERS

L1 STR



G1 N,Si,CH2

Structure attributes must be viewed using STN Express query preparation.

=> s l2

L2 NOT FOUND

The L-number entered has not been defined in this session, or it has been deleted. To see the L-numbers currently defined in this session, enter DISPLAY HISTORY at an arrow prompt (=>).

=> s l1

SAMPLE SEARCH INITIATED 12:44:54 FILE 'REGISTRY'

SAMPLE SCREEN SEARCH COMPLETED - 12 TO ITERATE

100.0% PROCESSED 12 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE \*\*COMPLETE\*\*

BATCH \*\*COMPLETE\*\*

PROJECTED ITERATIONS: 33 TO 447

PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 full

FULL SEARCH INITIATED 12:44:59 FILE 'REGISTRY'

FULL SCREEN SEARCH COMPLETED - 278 TO ITERATE

100.0% PROCESSED 278 ITERATIONS

0 ANSWERS

SEARCH TIME: 00.00.01

L3 0 SEA SSS FUL L1

FILE 'CAPLUS' ENTERED AT 12:47:55 ON 01 MAR 2005  
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FILE COVERS 1907 - 1 Mar 2005 VOL 142 ISS 10  
FILE LAST UPDATED: 28 Feb 2005 (20050228/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s tantalum amide  
85650 TANTALUM  
117846 AMIDE

L1 17 TANTALUM AMIDE  
(TANTALUM(W)AMIDE)

=> d 1-17 bib abs

L1 ANSWER 1 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2004:783724 CAPLUS

DN 141:424255

TI Zirconium, Hafnium, and **Tantalum Amide** Silyl

Complexes: Their Preparation and Conversion to Metallaheterocyclic Complexes via  $\gamma$ -Hydrogen Abstraction by Silyl Ligands

AU Yu, Xianghua; Bi, Siwei; Guzei, Ilia A.; Lin, Zhenyang; Xue, Zi-Ling

CS Departments of Chemistry, University of Tennessee, Knoxville, TN, 37996-1600, USA

SO Inorganic Chemistry (2004), 43(22), 7111-7119

CODEN: INOCAJ; ISSN: 0020-1669

PB American Chemical Society

DT Journal

LA English

OS CASREACT 141:424255

AB New transition metal silyl amide complexes  $(\text{Me}_2\text{N})_3\text{Ta}[\text{N}(\text{SiMe}_3)_2](\text{SiPh}_2\text{But})$  (1) and [cyclic]  $(\text{Me}_2\text{N})\text{M}[\text{N}(\text{SiMe}_3)_2]_2(\text{SiPh}_2\text{But})$  (M = Zr, 2a, and Hf, 2b) were found to undergo  $\gamma$ -H abstraction by the silyl ligands to give metallaheterocyclic complexes [cyclic]  $(\text{Me}_2\text{N})_3\text{Ta}(\text{NSiMe}_3\text{SiMe}_2\text{CH}_2)$  (3) and [cyclic]  $\{(\text{Me}_2\text{N})[(\text{Me}_3\text{Si})_2\text{N}]\text{M}(\text{NSiMe}_3\text{SiMe}_2\text{CH}_2)\}_2$  (M = Zr, 4a, and Hf, 4b), resp. The conversion of 1 to 3 follows first-order kinetics with  $\Delta H_{\text{thermod.}} = 23.6(1.6)$  kcal/mol and  $\Delta S_{\text{thermod.}} = 3(5)$  eu between 288 and 313 K. The formation of 4a from  $(\text{Me}_2\text{N})\text{Zr}[\text{N}(\text{SiMe}_3)_2]_2\text{Cl}$  (5a) and  $\text{Li}(\text{THF})_2\text{SiPh}_2\text{But}$  (6) involves the formation of the intermediate 2a, followed by  $\gamma$ -H abstraction. Kinetic studies of these consecutive reactions, a second-order reaction to give 2a and then a first-order  $\gamma$ -H abstraction to give 4a, were conducted by an anal. method and a numerical method. At 278 K, the rate consts.  $k_1$  and  $k_2$  for the two consecutive reactions are  $2.17(0.03) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  and  $5.80(0.15) \times 10^{-5} \text{ s}^{-1}$  by the anal. method. The current work is a rare kinetic study of the  $\text{A} + \text{B} \rightarrow \text{C} \rightarrow \text{D}$  (+ E) consecutive reactions. Kinetic studies of the formation of a metallaheterocyclic moiety  $\text{M}(\text{NSiMe}_3\text{SiMe}_2\text{CH}_2)$  have not been reported. In addition,  $\gamma$ -H abstraction by a silyl ligand to give such a metallaheterocyclic moiety is new. Theor. investigations of the  $\gamma$ -H abstraction by silyl ligands have been conducted by d. functional theory calcns. at the Becke3LYP

(B3LYP) level, and they revealed that the formation of the metallacyclic complexes through  $\gamma$ -H abstraction is entropically driven. X-ray crystal structures of  $(\text{Me}_2\text{N})_3\text{Ta}[\text{N}(\text{SiMe}_3)_2](\text{SiPh}_2\text{But})$  (1),  $(\text{Me}_2\text{N})\text{Zr}[\text{N}(\text{SiMe}_3)_2]_2\text{Cl}$  (5a), and [cyclic]  $\{(\text{Me}_2\text{N})[(\text{Me}_3\text{Si})_2\text{N}]\text{M}(\text{NSiMe}_3\text{SiMe}_2\text{CH}_2)\}_2$  (M = Zr, 4a, and Hf, 4b) are also reported.

RE.CNT 91 THERE ARE 91 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 2 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2003:784913 CAPLUS

DN 139:396019

TI Structure, Bonding, and Reactivity of Tantalum Amides Containing o-Naphthyl- and o-Indenylphenoxide Ligation

AU Thorn, Matthew G.; Parker, Jennifer R.; Fanwick, Phillip E.; Rothwell, Ian P.

CS Department of Chemistry, Purdue University, West Lafayette, IN, 47907-2038, USA

SO Organometallics (2003), 22(23), 4658-4664

CODEN: ORGND7; ISSN: 0276-7333

PB American Chemical Society

DT Journal

LA English

OS CASREACT 139:396019

AB The reaction of  $[\text{Ta}(\text{NMe}_2)_5]$  with the o-(2,3-dihydro-1-naphthyl)-, o-(1-naphthyl)-, and o-(inden-3-yl)phenols  $[\text{HOC}_6\text{H}_2\text{Ar}-2\text{-But}_{2-4,6}]$  (Ar =  $\text{C}_{10}\text{H}_9$ ,  $\text{C}_{10}\text{H}_7$  (Np),  $\text{C}_9\text{H}_7$ ) has been investigated. In all three cases initial displacement of 1 equivalent of dimethylamine occurs, yielding mono(aryloxides)  $[(\text{ArO})\text{Ta}(\text{NMe}_2)_4]$ . Structural studies of the o-(2,3-dihydro-1-naphthyl) and o-(1-naphthyl) compds. 4 and 5 show they both adopt geometries best described as square pyramidal with an apical dimethylamido ligand and basal aryloxide oxygen. The Ta-O-Ar angles are  $162^\circ$  in both compds., with no metal interaction with the ortho substituents. Compound 4 reacts with 2,3,5,6-tetraphenylphenol to form the corresponding bis(aryloxide) 6. The intermediate o-(inden-3-yl)phenoxide  $[(\text{ArO})\text{Ta}(\text{NMe}_2)_4]$  7 thermally eliminates a further 1 equivalent of  $\text{HNMe}_2$  with formation of the tris(amido) compound  $[\text{Ta}(\text{OC}_6\text{H}_2\{\eta^1\text{-Ind}\}-2\text{-But}_{4,6})(\text{NMe}_2)_3]$  8. The coordination geometry about tantalum in 8 is best described as trigonal bipyramidal, with an oxygen and amido group in the axial positions: O-Ta-N =  $170^\circ$ . The carbon atom of the indenyl ring bound directly to the phenoxide nucleus is metalated, leading to a five-membered metalacycle. Hence, both deprotonation (CH bond activation) and tautomerization of the original inden-3-yl ring has occurred. The Ta-C(121) distance of 2.285(9) Å is consistent with an  $\eta^1$ -indenyl ring being present in 8. Replacement of the dimethylamido ligands in 8 by chloride groups was achieved by reaction with  $\text{SiCl}_4$ . Structural anal. of the 4-phenylpyridine adduct  $[\text{Ta}(\text{OC}_6\text{H}_2\{\eta^3\text{-Ind}\}-2\text{-But}_{4,6})(\text{NC}_5\text{H}_4\text{Ph}-4)\text{Cl}_3]$  9 showed the presence of an  $\eta^3$ -indenyl interaction with the tantalum metal center. The bonding parameters for the  $\eta^1$ - and  $\eta^3$ -indenyl rings are compared with those of related  $\eta^5$ -cyclopentadienyl derivs. of niobium and tantalum.

RE.CNT 38 THERE ARE 38 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 3 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2003:613851 CAPLUS

DN 140:223914

TI Dinuclear activation in sterically-hindered three-coordinate transition metal complexes

AU Christian, Gemma; Driver, Jenni; Stranger, Robert

CS Department of Chemistry, The Australian National University, Canberra, 0200, Australia

SO Faraday Discussions (2003), 124, 331-341

CODEN: FDISE6; ISSN: 1359-6640

PB Royal Society of Chemistry

DT Journal

LA English

AB Dinuclear metal systems based on sterically-hindered, three-coordinate transition metal complexes of the type  $\text{ML}_3$  where the ancillary ligands L

comprise bulky organic substituents, hold great promise synthetically for the activation and scission of small, multiply-bonded mols. such as N<sub>2</sub>, NO and N<sub>2</sub>O. In this study we have employed d. functional methods to identify the metal/ligand combinations which achieve optimum activation and/or cleavage of N<sub>2</sub>. Strong  $\pi$  donor ligands such as NH<sub>2</sub> and OH are found to produce the greatest level of activation based on N-N bond lengths in the intermediate dimer complex, L<sub>3</sub>Mo( $\mu$ -N<sub>2</sub>)MoL<sub>3</sub>, whereas systems containing the weak or non- $\pi$  donor ligands NH<sub>3</sub>, PH<sub>3</sub>, OH<sub>2</sub> and SH<sub>2</sub> are found to be thermodynamically unfavorable for N<sub>2</sub> activation. In the case of the Mo-NH<sub>2</sub> and W-NH<sub>2</sub> systems, a fragment bonding anal. reveals that the orientation of the amide ligands around the metal is important in determining both the spin state and the extent of dinitrogen activation in the intermediate dimer. For both systems, an intermediate dimer structure where one of the NH<sub>2</sub> ligands on each metal is rotated 90° relative to the other ligands, is more activated than the structure in which the NH<sub>2</sub> ligands are trigonally disposed around the metals. The level of activation is found to be very sensitive to the electronic configuration of the metal with d<sup>3</sup> metal ions delivering the best activation along any one transition series. In particular, strong activation or cleavage of N<sub>2</sub> was calculated for the third row d<sup>3</sup> metals systems involving Ta(II), W(III) and Re(IVa), with the level of activation decreasing as the nuclear charge on the metal increases. This trend in activation reflects the size of the valence 5d orbitals and consequently, the capacity of the metal to back donate into the dinitrogen  $\pi^*$  orbitals.

RE.CNT 22 THERE ARE 22 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 4 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
AN 2002:834154 CAPLUS  
DN 138:205163  
TI Competitive insertion of isocyanide into tantalum - amido and tantalum - methyl bonds  
AU Amor, Francisco; Sanchez-Nieves, Javier; Royo, Pascual; Jacobsen, Heiko; Blacque, Olivier; Berke, Heinz; Lanfranchi, Maurizio; Pellinghelli, Maria Angela; Tiripicchio, Antonio  
CS Departamento de Quimica Inorganica, Universidad de Alcala, Alcala de Henares, 28871, Spain  
SO European Journal of Inorganic Chemistry (2002), (11), 2810-2817  
CODEN: EJICFO; ISSN: 1434-1948  
PB Wiley-VCH Verlag GmbH & Co. KGaA  
DT Journal  
LA English  
OS CASREACT 138:205163  
AB The (amido)methyl complexes [Cp\*Ta(NtBu)Me(NR<sub>2</sub>)] [Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; R = Ph (3), SiMe<sub>3</sub> (4)] were prepared by reaction of [Cp\*Ta(NtBu)ClMe] (1) with the appropriate lithium amides. Attempts to isolate the analogous NHMe derivative afforded a mixture of complexes [Cp\*Ta(NtBu)Me(NHMe)] (5) and [Cp\*Ta(NMe)Me(NHtBu)] (6), resulting from hydrogen exchange between the amido and imido ligands. Complexes 5 and 6 are not interconverting in THF solution in NMR time scale. Insertion of CN(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) into the Ta-Me bond of complexes 3 and 4 gave the  $\eta^1$ -iminoacyl derivs. [Cp\*Ta(NtBu)(NR<sub>2</sub>){ $\eta^1$ -C(Me)=N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}] [R = Ph (7), SiMe<sub>3</sub> (8)]. The same reaction of the complexes [Cp\*Ta(NtBu)Me(NRMe)] [R = H (5), Me (2)] proceeds as insertion into the Ta-NRMe bond and gave the  $\eta^2$ -iminocarbamoyl compds. [Cp\*Ta(NtBu)Me( $\eta^2$ -C(NRMe)=N(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>))] (10, 9, resp.). All of the new compds. were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The x-ray crystal structure of 9 is reported. DFT calcns. were carried out to justify the preference of the insertion either into the Ta-C or the Ta-N bond.

RE.CNT 55 THERE ARE 55 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 5 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
AN 2002:617671 CAPLUS  
TI Synthesis and characterization of a **tantalum amide** hydride complex from the reaction of a **tantalum amide** with silane  
AU Cai, Hu; Chen, Tianniu; Xue, Zi-Ling

CS Department of Chemistry, University of Tennessee, Knoxville, TN,  
37996-1600, USA

SO Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United  
States, August 18-22, 2002 (2002), INOR-519 Publisher: American Chemical  
Society, Washington, D. C.  
CODEN: 69CZPZ

DT Conference; Meeting Abstract

LA English

AB The reaction of [(Me<sub>2</sub>N)<sub>3</sub>TaCl<sub>2</sub>]<sub>2</sub> with LiN(SiMe<sub>3</sub>)<sub>2</sub> yields  
(Me<sub>2</sub>N)<sub>3</sub>Ta[μ-CH<sub>2</sub>Si(Me)<sub>2</sub>NSiMe<sub>3</sub>] (1) quant. 1 was found to react with  
H<sub>3</sub>SiPh to yield dinuclear tantalum amido hydride 2. Our studies of these  
reactions and characterization of 1 and 2 are presented.

L1 ANSWER 6 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2001:639421 CAPLUS

TI New amide silyl and disilyl complexes of tantalum(V)

AU Xue, Ziling; Wu, Zhongzhi; Diminnie, Jonathon B.

CS Department of Chemistry, University of Tennessee, Knoxville, TN, 37996,  
USA

SO Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United  
States, August 26-30, 2001 (2001), INOR-234 Publisher: American Chemical  
Society, Washington, D. C.  
CODEN: 69BUZP

DT Conference; Meeting Abstract

LA English

AB **Tantalum amide** silyl and bis(silyl) complexes  
(Me<sub>2</sub>N)<sub>3</sub>Ta(SiR<sub>3</sub>)Cl [SiR<sub>3</sub>=Si(SiMe<sub>3</sub>)<sub>3</sub> (1), SiPh<sub>2</sub>But (2)], (Me<sub>2</sub>N)<sub>4</sub>Ta(SiR<sub>3</sub>)  
[SiR<sub>3</sub>=Si(SiMe<sub>3</sub>)<sub>3</sub> (3), SiPh<sub>2</sub>But (4)], (Me<sub>2</sub>N)<sub>3</sub>Ta(SiPh<sub>2</sub>But)<sub>2</sub> (5), and  
(Me<sub>2</sub>N)<sub>3</sub>Ta(SiPh<sub>2</sub>But)[Si(SiMe<sub>3</sub>)<sub>3</sub>] (6) have been prepared and characterized. 3  
reacts with one equiv of O<sub>2</sub> to give (Me<sub>2</sub>N)<sub>3</sub>Ta(η<sup>2</sup>-ONMe<sub>2</sub>)[OSi(SiMe<sub>3</sub>)<sub>3</sub>]  
(7). The spectroscopic data of 1-6 and crystal structures of 1, 2 and 4  
reveal that the coordination geometry around Ta atoms is trigonal  
bipyramid with silyl ligands in the equatorial position in 1-4 and in the  
axial position in 5-6, resp.

L1 ANSWER 7 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2001:541456 CAPLUS

DN 135:331512

TI Synthesis of isomeric B-methylated tantalum carboranes, (Me<sub>2</sub>N)<sub>3</sub>TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>Me

AU Fox, Mark A.; Howard, Judith A. K.; Hughes, Andrew K.; Malget, John M.;  
Yufit, Dimitrii S.

CS Department of Chemistry, University of Durham, Durham, DH1 3LE, UK

SO Journal of the Chemical Society, Dalton Transactions (2001), (15),  
2263-2269  
CODEN: JCSDA; ISSN: 1472-7773

PB Royal Society of Chemistry

DT Journal

LA English

OS CASREACT 135:331512

AB The cage-alkylated metallacarborane complex [4,4,4-(NMe<sub>2</sub>)<sub>3</sub>-3-Me-4,1,2-  
closo-TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (8), was obtained as the only product from the reaction  
of Ta(NMe<sub>2</sub>)<sub>5</sub> with nido-11-Me-2,7-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>, which is prone to skeletal  
rearrangement under basic conditions. That no rearrangement occurs  
indicates that the hydroaminolysis reaction is a clean synthetic method.  
The isomeric metallacarboranes [3,3,3-(NMe<sub>2</sub>)<sub>3</sub>-4-Me-3,1,2-closo-TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]  
(9) and [2,2,2-(NMe<sub>2</sub>)<sub>3</sub>-3-Me-2,1,7-closo-TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (10) were produced from  
the reaction of Ta(NMe<sub>2</sub>)<sub>5</sub> with [Me<sub>3</sub>NH][nido-9-Me-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] and  
[Me<sub>3</sub>NH][nido-8-Me-7,9-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], resp. Identities of the metallacarboranes  
8, 9 and 10 were deduced by detailed multinuclear (11B, 13C and 1H) NMR  
spectroscopy. These geometries are supported by B NMR shift predictions  
based on observed shifts of the known non-methylated analogs  
[3,3,3-(NMe<sub>2</sub>)<sub>3</sub>-closo-3,1,2-TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] and [3,3,3-(NMe<sub>2</sub>)<sub>3</sub>-closo-2,1,7-  
TaC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] and calculated shifts (GIAO-B3LYP/6-311G\*/MP2/6-31G\*) of the B-Me  
carboranes, closo-3-Me-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>, 4-Me-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub> and  
2-Me-1,7-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>. The mol. structure of 8 was determined by x-ray  
diffraction.

RE.CNT 78 THERE ARE 78 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 8 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2001:194211 CAPLUS

DN 135:19719

TI Insertion of carbon dioxide and isocyanide into **tantalum-**  
**amide** and tantalum-methyl bonds

AU Sanchez-Nieves, J.; Royo, P.

CS Departamento de Quimica Inorganica, Facultad de Ciencias, Campus  
Universitario, Universidad de Alcala, Alcala de Henares, E-28871, Spain

SO Journal of Organometallic Chemistry (2001), 621(1-2), 299-303

CODEN: JORCAI; ISSN: 0022-328X

PB Elsevier Science S.A.

DT Journal

LA English

OS CASREACT 135:19719

AB The Me-amide complex [TaCp\*(NtBu)Me(NMe2)] (1a) was isolated by reaction  
of the chloro-Me [TaCp\*(NtBu)MeCl] complex with LiNMe2. Reaction of the  
mono-amide compds. [TaCp\*(NtBu)XY] (X = NMe2, Y = Me (1a); X = NHtBu, Y =  
Me (1b), Cl (1c)) with CO2 gives the  $\eta^2$ -carbamate derivs.

[TaCp\*(NtBu)( $\eta^2$ -O2CX)Y] (X = NMe2, Y = Me (2a); X = NHtBu, Y = Me

(2b), Cl (2c)). A similar reaction with the di-amide complex

[TaCp\*(NtBu)(NHtBu)2] (1d) gives the di-carbamate derivative

[TaCp\*(NtBu){ $\eta^2$ -O2C(NHtBu)}{ $\eta^1$ -O2C(NHtBu)}] (2d). Reaction of the

Me-carbamate (2a) with isocyanide CNAr (Ar = 2,6-Me2C6H3) gives the

$\eta^2$ -iminoacyl- $\eta^1$ -carbamate complex [TaCp\*(NtBu){ $\eta^2$ -

C(Me):NAr}{ $\eta^1$ -O2C(NMe2)}] (3a). Formation of the related compound

[TaCp\*(NtBu){ $\eta^2$ -C(Me):NAr}{ $\eta^1$ -O2C(NHtBu)}] (3b) was only detected

by NMR spectroscopy in C6D6 or CDCl3 whereas the reaction of 2b in hexane

gives the  $\eta^1$ -iminoacyl- $\eta^2$ -carbamate complex [TaCp\*(NtBu){ $\eta^1$ -

C(Me):NAr}{ $\eta^2$ -O2C(NHtBu)}] (3b').

RE.CNT 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 9 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 2000:732659 CAPLUS

DN 134:100959

TI Insertion and cleavage reactions of [closo-3,1,2-Ta(NMe2)3(C2B9H11)] with  
nitriles, phenols and thiols; structural characterization of  
N,N-dimethylamidinate ligands

AU Broder, Charlotte K.; Goeta, Andres E.; Howard, Judith A. K.; Hughes,  
Andrew K.; Johnson, Andrew L.; Malget, John M.; Wade, Ken

CS Department of Chemistry, University Science Laboratories, Durham, DH1 3LE,  
UK

SO Dalton (2000), (20), 3526-3533

CODEN: DALTFG

PB Royal Society of Chemistry

DT Journal

LA English

OS CASREACT 134:100959

AB The Ta complex [closo-3,1,2-Ta(NMe2)3(C2B9H11)] underwent insertion into  
the N-Ta bond by MeCN and p-fluorobenzonitrile to give the  
N,N-dimethylacetamidinate complex [closo-3,1,2-Ta{N:C(Me)NMe2}3(C2B9H11)],  
and p-fluoro-N,N-dimethylbenzamidinate complex, [closo-3,1,2-  
Ta{N:C(C6H4F)NMe2}3(C2B9H11)], resp. Attempted recrystn. of the latter  
from chlorinated solvents led to [closo-3,1,2-  
Ta{N:C(C6H4F)NMe2}2Cl(C2B9H11)], in which one amidinate ligand was  
replaced by a chloride. [Closo-3,1,2-Ta(NMe2)3(C2B9H11)] reacts with  
cyclohexyl isocyanide to give [Ta(NMe2)2( $\eta^2$ -N(Cy)CNMe2)(C2B9H11)].  
The structures of the novel N,N-dialkylamidinate complexes were determined by  
single crystal x-ray diffraction, and reveal the extensive delocalization  
and strong  $\pi$ -donor character of the amidinate ligands. The M-N bonds  
of [closo-3,1,2-Ta(NMe2)3(C2B9H11)] are cleaved by protic reagents, and it  
reacts with 2,6-dimethylphenol to give [closo-3,1,2-Ta(OC6H3Me2-  
2,6)3(C2B9H11)] and with benzenethiol to give the charge-compensated  
complex [closo-3-Ta(SC6H5)4(9-NHMe2-1,2-C2B9H10)] where the  $\beta$ -B of  
the C2B3 face bears an NHMe2+ substituent. The structures of the last two  
compds. also were determined by x-ray crystallog.

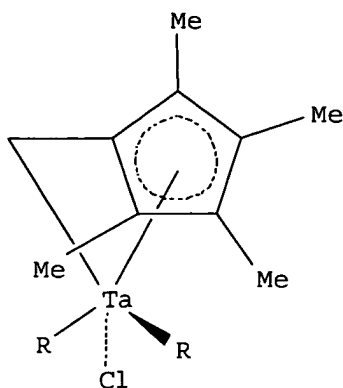
RE.CNT 80 THERE ARE 80 CITED REFERENCES AVAILABLE FOR THIS RECORD

## ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 10 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
AN 1999:688374 CAPLUS  
DN 132:122706  
TI Transition metal dicarbollide complexes: synthesis, molecular, crystal and electronic structures of  $[M(C_2B_9H_{11})(NMe_2)_3]$  ( $M = Nb$  or  $Ta$ ) and their insertion reactions with  $CO_2$  and  $CS_2$   
AU Batsanov, Andrei S.; Churakov, Andrei V.; Howard, Judith A. K.; Hughes, Andrew K.; Johnson, Andrew L.; Kingsley, Andrew J.; Neretin, Ivan S.; Wade, Ken  
CS Department of Chemistry, University of Durham, Durham, DH1 3LE, UK  
SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1999), (21), 3867-3875  
CODEN: JCDTBI; ISSN: 0300-9246  
PB Royal Society of Chemistry  
DT Journal  
LA English  
AB The homoleptic amides  $[M(NMe_2)_5]$  ( $M = Nb$  1 or  $Ta$  2; the latter is characterized by a structural study) reacted with the carborane nido- $C_2B_9H_{13}$  to eliminate two equivalent of  $HNMe_2$  and generate the dicarbollide half-sandwich tris(dimethylamide) complexes  $[M(C_2B_9H_{11})(NMe_2)_3]$  ( $M = Nb$  3 or  $Ta$  4). The crystal structures of isomorphous 3 and 4 were determined and reveal two  $NMe_2$  ligands in a vertical orientation and the 3rd one in a horizontal orientation with respect to the  $\eta^5$ -coordinated face of the  $C_2B_9H_{11}$  ligand. The electronic factors responsible for the amide ligand orientations in these complexes are explored using qual. MO arguments. Complexes 3 and 4 reacted with  $CO_2$  and  $CS_2$  to yield the tris(carbamate)  $[M(C_2B_9H_{11})(O_2CNMe_2)_3]$  ( $M = Nb$  5 or  $Ta$  7) and tris(dithiocarbamate)  $[M(C_2B_9H_{11})(S_2CNMe_2)_3]$  ( $M = Nb$  6 or  $Ta$  8) complexes, resp. The crystal structures of 6 and 7 show two (dithio)carbamate ligands in horizontal and one in vertical orientation, demonstrating the similarity between the  $\sigma, \pi$ -donor frontier orbitals of the ligands  $NMe_2$  and  $X_2CNMe_2$  in 4 and 6 or 7 resp.  
RE.CNT 37 THERE ARE 37 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 11 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
AN 1999:503003 CAPLUS  
DN 131:257662  
TI Formation of Tantalum "Tuck-in" Complexes by Activation of Methyl C-H Bonds in Pentamethylcyclopentadiene Groups by Carbazole Ligation  
AU Riley, Patrick N.; Parker, Jennifer R.; Fanwick, Phillip E.; Rothwell, Ian P.  
CS Department of Chemistry, Purdue University, West Lafayette, IN, 47907-1393, USA  
SO Organometallics (1999), 18(18), 3579-3583  
CODEN: ORGND7; ISSN: 0276-7333  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 131:257662  
GI





I

AB The reaction of  $[\text{Cp}^*\text{TaCl}_4]$  with the K salt of carbazole (cbK, >3 equiv) in hydrocarbon solvents leads to  $[(\text{C}_5\text{Me}_4\text{CH}_2)\text{Ta}(\text{cb})_2\text{Cl}]$  (1; shown as I, R = cb), in which one of the ring Me C-H bonds of the  $\text{Cp}^*$  ligand was cleaved along with free cbH. Spectroscopic and structural studies of 1 show a lack of a plane of symmetry through the mol. with nonequivalent cb ligands. A minor component of the reaction mixture is believed to be the substitutional isomer in which both carbazole ligands are equivalent. Alkylation of 1 with  $\text{LiCH}_2\text{SiMe}_3$  or  $\text{PhCH}_2\text{MgCl}$  generates the corresponding monoalkyl derivs.  $[(\text{C}_5\text{Me}_4\text{CH}_2)\text{Ta}(\text{cb})_2(\text{R})]$  (7 or 8, resp.). Structural studies of 1, 7, and 8 support an  $\eta^1:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$  ( $\sigma:\eta^5\text{-CH}_2\text{C}_5\text{Me}_4$ ) description for the metalated ligands, with significant slippage toward an  $\eta^1:\eta^3\text{-CH}_2\text{C}_5\text{Me}_4$  resonance form. To compare the extent of  $\pi$ -bonding between cb and dialkylamido ligands,  $[(\text{cb})_2\text{Ta}(\text{NMe}_2)_3]$  (9) was synthesized and structurally characterized. The mol. structure of 9 consists of a *tdp* arrangement of N atoms with trans, axial cb ligands. The Ta-cb distances are 0.2 Å longer than the Ta-NMe<sub>2</sub> distances. An improved (safer) procedure for the synthesis of  $[\text{Ta}(\text{NMe}_2)_5]$  is presented.

RE.CNT 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 12 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1998:577563 CAPLUS

DN 129:247356

TI Reduced Variational Space Analysis of Methane Adducts

AU Cundari, Thomas R.; Klinckman, Thomas R.

CS Department of Chemistry, The University of Memphis, Memphis, TN, 38152-6060, USA

SO Inorganic Chemistry (1998), 37(20), 5399-5401

CODEN: INOCAJ; ISSN: 0020-1669

PB American Chemical Society

DT Journal

LA English

AB An anal. of the binding of methane to transition metal complexes using the RVS-SCF (Reduced Variational Space-Self Consistent Field) technique was reported in order to optimize binding of methane to transition metal complexes for selective functionalization. Three energetic components dominate the binding of methane to the metal complex: Coulomb and exchange repulsion, polarization of methane, and charge transfer from methane to the metal complex. While the latter two are stabilizing interactions, energetic changes in the Coulomb and exchange repulsion are largely counterbalanced by changes in the methane polarization component. Trends as a function of metal, ligand, and charge on the methane binding energy are largely due to changes in the degree of charge transfer from methane to the metal complex.

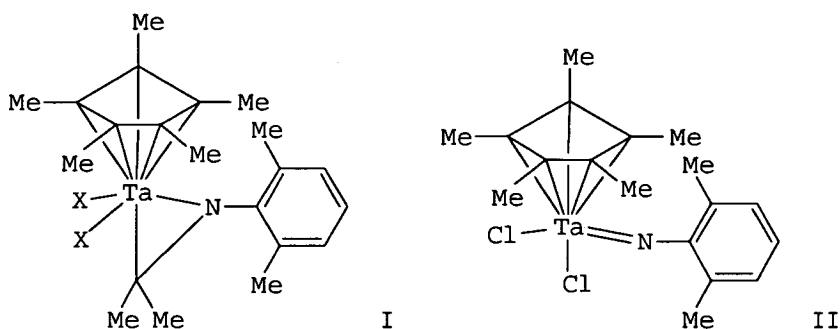
RE.CNT 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L1 ANSWER 13 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1994:409552 CAPLUS

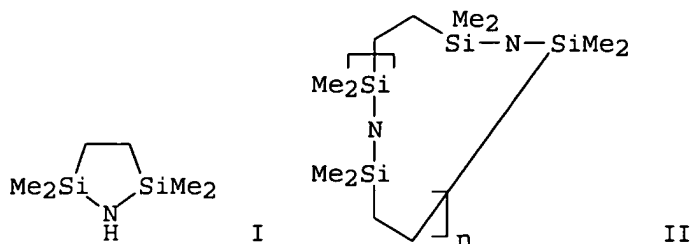
DN 121:9552

TI Insertion of CNAr into Ta-Me bonds of TaCp\*Cl<sub>n</sub>Me<sub>4-n</sub> (n = 0-3):  
 intramolecular rearrangements, dynamic behavior, and x-ray crystal  
 structure of TaCp\*Cl<sub>2</sub>(NAr) (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)  
 AU Galakhov, Mikhail V.; Gomez, Manuel; Jimenez, Gerardo; Pellinghelli, Maria  
 Angela; Royo, Pascual; Tiripicchio, Antonio  
 CS Departamento de Quimica Inorganica, Universidad de Alcala, Alcala de  
 Henares, E-28871, Spain  
 SO Organometallics (1994), 13(5), 1564-6  
 CODEN: ORGND7; ISSN: 0276-7333  
 DT Journal  
 LA English  
 OS CASREACT 121:9552  
 GI



AB The dimethyltantalum complex TaCp\*Cl<sub>2</sub>Me<sub>2</sub> (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) reacts  
 readily with isocyanide, CNAr (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), to form the  
 azatantalacyclopropane derivative TaCp\*Cl<sub>2</sub>(η<sup>2</sup>-NArCMe<sub>2</sub>) (1; shown as I, X =  
 Cl), which can be alkylated with 2 equiv LiMe to give the di-Me complex  
 TaCp\*Me<sub>2</sub>(η<sup>2</sup>-NArCMe<sub>2</sub>) (2; shown as I, X = Me). Reaction of 1 and 2  
 with an addnl. 1 equiv of isocyanide leads to the imido complexes  
 TaCp\*Cl<sub>2</sub>(NAr) (3; shown as II) and TaCp\*Me(NArCMe:CMe<sub>2</sub>)(NAr) (5), resp.  
 Complex 5 is also obtained by reaction of TaCp\*Me<sub>4</sub> with 2 equiv of  
 isocyanide, and the same reaction with TaCp\*ClMe<sub>3</sub> leads to  
 TaCp\*Cl(NArCMe:CMe<sub>2</sub>)(NAr) (4). The complexes were characterized by NMR  
 studies (<sup>1</sup>H, <sup>13</sup>C, and <sup>13</sup>C CP/MAS), and the crystal structure of complex 3  
 was determined by x-ray crystallog. The dynamic behavior of complexes 1, 2, 4,  
 and 5 was studied in solution, and kinetic parameters were calculated from <sup>1</sup>H  
 DNMR data.

L1 ANSWER 14 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
 AN 1993:51166 CAPLUS  
 DN 118:51166  
 TI Multiple bonds between main group elements and transition metals. CXX.  
 Niobium and **tantalum amide** complexes and new  
 cyclocarbodisilazanes  
 AU Herrmann, Wolfgang A.; Dvckhoff, Florian; Herdtweck, Eberhardt  
 CS Anorg.-Chem. Inst., Tech. Univ. Muenchen, Garching, D-8046, Germany  
 SO Chemische Berichte (1992), 125(12), 2651-6  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DT Journal  
 LA German  
 GI



AB L3M:O (M = Nb, Ta; HL = I) are accessible by the reaction of  $\text{MOCl}_3$  with  $\text{LLi}$  in 30 and 19% isolated yield, resp. The new silazanes II ( $n = 2, 3$ ) are prepared from  $\text{Me}_2\text{ClSiCH}_2\text{CH}_2\text{SiClMe}_2$  and  $\text{NH}_3$ . The structures of II ( $n = 2, 3$ ) were determined by single-crystal structure analyses.

L1 ANSWER 15 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1991:128189 CAPLUS

DN 114:128189

TI **Tantalum amide** preparation

AU Chestnut, Robert W.; Rothwell, Ian P.; Holl, Mark Banaszak; Wolczanski, Peter T.

CS Purdue Univ., IN, USA

SO Chemical & Engineering News (1990), 68(31), 2

CODEN: CENEAR; ISSN: 0009-2347

DT Journal

LA English

AB Explosions of  $\text{LiNMe}_2$ - $\text{TaCl}_5$  mixts. can be avoided in the preparation of pentakisdimethylamidotantalum by the  $\text{TaCl}_5$  addition to a slurry of  $\text{LiNMe}_2$  in pentane method by D. C. Bradley and M. Thomas, Can. J. Chemical, 40, 1355 (1962).  $\text{LiNMe}_2$  should be prepared in situ using excess  $\text{HNMe}_2$ . The reaction will proceed smoothly using a pentane/diethyl ether solvent mixture (50/50).

L1 ANSWER 16 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN

AN 1988:476196 CAPLUS

DN 109:76196

TI Transition metal carbides and process for making same

IN Laine, Richard M.

PA SRI International, USA

SO PCT Int. Appl., 18 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 4

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 8801603	A1	19880310	WO 1987-US2057	19870820
	W: JP				
	RW: AT, BE, CH, DE, FR, GB, IT, LU, NL, SE				
	EP 278970	A1	19880824	EP 1987-905851	19870820
	EP 278970	B1	19930407		
	R: BE, DE, FR, GB, IT, NL				
	JP 01502427	T2	19890824	JP 1987-505447	19870820
	CA 1313938	A1	19930302	CA 1987-545246	19870825
PRAI	US 1986-900592	A	19860826		
	WO 1987-US2057	W	19870820		

OS MARPAT 109:76196

AB The title carbides are manufactured by a process comprising pyrolyzing a tractable transition metal amide of the formula  $\text{M}_x(\text{NR}_1\text{R}_2)_y$  (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Hf, Ta, W, Re, Os, Ir, Pt, and all elements having atomic no  $\geq 89$ ;  $x \geq 2$ ;  $\text{R}_{1,2} = \text{H}$ , lower alkyl, trimethylsilyl,  $\text{C}_2\text{H}_5$ , but cannot both be H; Y = integer equal to valence of Mx), under nonoxidizing conditions at a temperature at which a C-containing group or amido group of the amide undergoes chemical reactions with a metal atom of the amide to form  $\geq 1$  covalent C-metal bonds. These carbides are used in making a variety of hard and/or high-temperature materials at low temps. Ni-coated stainless steel tubes were charged with 0.07 g

W2(NMe2)6 under Ar, N, or NH3, and pyrolyzed at 800° for 25 min.  
The product had the crystal structure of hexagonal W2C3.

L1 ANSWER 17 OF 17 CAPLUS COPYRIGHT 2005 ACS on STN  
AN 1979:65850 CAPLUS  
DN 90:65850  
TI Structure and reactivity in the group 5B tert-butylimido complexes  
(Me2N)3M=NCMe3; x-ray crystal and molecular structure of  
N-tert-butylimidotris(dimethylamido)tantalum  
AU Nugent, William A.; Harlow, Richard L.  
CS Cent. Res. Dev. Dep., E. I. du Pont de Nemours and Co., Wilmington, DE,  
USA  
SO Journal of the Chemical Society, Chemical Communications (1978), (14),  
579-80  
CODEN: JCCCAT; ISSN: 0022-4936  
DT Journal  
LA English  
AB MCl5 (M = Nb, Ta) reacted with LiNMe2 and LiNHCMMe3 to give (Me2N)3M:NCMe3  
which were characterized by NMR spectra and extended Hueckel MO calcns.  
Ta(NMe2)5 with Me3CNH2 also gave (Me2N)3Ta:NCMe3. The complexes underwent  
typical reactions of the dialkylamide ligands with electrophiles, e.g.  
Ph2CO. There is a linear M:N-C unit in each complex; the M:N bond of 1.77  
Å is the longest known. The crystal and mol. structure of  
(Me2N)3Ta:NCMe3 was determined from x-ray diffractometer data by the heavy atom  
method and refined by least squares to R 0.076 for 1017 observed reflections.  
The Me groups of the NCMe3 moiety are disordered about the 3-fold axis.

(FILE 'HOME' ENTERED AT 12:47:42 ON 01 MAR 2005)

FILE 'CAPLUS' ENTERED AT 12:47:55 ON 01 MAR 2005

L1 17 S TANTALUM AMIDE

=> s "bis-diethylamino-tris-dimethylaminotantalum"

450536 "BIS"

30073 "DIETHYLAMINO"

114799 "TRIS"

0 "DIMETHYLAMINOTANTALUM"

L2 0 "BIS-DIETHYLAMINO-TRIS-DIMETHYLAMINOTANTALUM"

("BIS" (W) "DIETHYLAMINO" (W) "TRIS" (W) "DIMETHYLAMINOTANTALUM")